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**COMMENTS ON "CONTACT DIFFUSION
INTERACTION OF MATERIALS
WITH CLADDING"**

by James F. Morris

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COMMENTS ON "CONTACT DIFFUSION INTERACTION OF MATERIALS WITH CLADDING"

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SUMMARY

A Russian paper by A. A. Babad-Zakhryapina contributes much to the understanding of fuel, clad interactions and thus to nuclear thermionic technology. In that publication the basic diffusion expression is a simple one. A more general but complicated equation for this mass transport results from the present work. With appropriate assumptions, however, the new relation reduces to Babad-Zakhryapina's version.

A REACTOR MASS-TRANSPORT PROBLEM

A major complication in nuclear power generators is the intermingling and reaction of the fuel with its immediate container. When the restraining wall is an essential part of the energy converter itself, this physicochemical interchange affects the output and life of the system directly. Then it becomes a crucial problem - as it is for in-core thermionics.

Reference 1 focuses analytically and experimentally on part of this technical area, the "contact diffusion interaction of materials with cladding." Through close theoretic and empiric coordination of its results, that publication adds substantially to the knowledge of mass transport in the reactor. In the first two sections Babad-Zakhryapina develops the model and a simple diffusion equation to serve as the basis for further analyses. That initial presentation appears in this report in the appendix to assist the reader and to obviate repeating the detailed introduction.

The present derivation begins with the assumptions of reference 1 and produces a less approximate expression for the migration of fuel components through clads. Then a comparison of the new and the old descriptions indicates the applicability of Babad-Zakhryapina's version.

A MORE GENERAL DIFFUSION EQUATION

The basic fuel, clad diffusion problem is that outlined by Babad-Zakhryapina and quoted in the appendix. The solution sought is one for "low values of k and t ," as well as for very small $x \leq l = kt$.

But before the new derivation a comment on the referenced one seems in order: The integral version of equation (A3) applies only for the location $x = l$, where $dx/dt = dl/dt = k$ and $\partial c/\partial x = \partial c/\partial l$. Here $c(x, t) = c_A = c(l, t) = c(kt, t) = c(t)_{x=l}$. And the fully developed differential expression is

$$\frac{D}{k} \frac{dc(t)_{x=l}}{dt} = \frac{D}{k} \frac{dc_A}{dt} = c_A k \quad (1)$$

So equation (A4) really becomes

$$c_A = c_0 \exp\left(\frac{-k^2 t}{D}\right) = c_0 \exp\left(\frac{-kl}{D}\right) \quad (2)$$

It describes the composition at the surface of the growing layer only - not the space, time variations of concentrations throughout the lamina. These effects are the objects of the following development.

First from

$$\frac{\partial c}{\partial t} = D \nabla^2 c \quad (3)$$

by Laplace transformation comes

$$sc(x, s) = D \frac{\partial^2 c(x, s)}{\partial x^2} \quad (4)$$

Then,

$$c(x, s) = c(0, s) \exp -x \sqrt{\frac{s}{D}} \quad (5)$$

Obviously $c(0, t)$ is $c(0, 0) f(t)$, but $f(t)$ hides effectively behind indefinite boundary conditions.

However, because k and t are slight, yet large compared with x , a "small system" approximation is possible (ref. 2). There, near homogeneity holds allowing separation of the variables:

$$c(c, t) \approx X(x)T(t) \quad (6)$$

Then Fick's second law becomes

$$\frac{1}{DT} \frac{dT}{dt} \approx \frac{1}{X} \left(\frac{d^2 X}{dx^2} \right) \quad (7)$$

But this can hold only if each side equals a constant, $-\lambda^2$. Thus,

$$T = T_0 \exp(-\lambda^2 Dt) \quad (8)$$

results with

$$X = A' \sin \lambda x + B' \cos \lambda x \quad (9)$$

So the particular solution is

$$c(x, t) \approx (A \sin \lambda x + B \cos \lambda x) \exp(-\lambda^2 Dt) \quad (10)$$

and the general expression is

$$c(x, t) \approx \sum_{n=1}^{\infty} (A_n \sin \lambda_n x + B_n \cos \lambda_n x) \exp(-\lambda_n^2 Dt) \quad (11)$$

For an approximate thin-film approach, though, the simplified solution suffices. As $k \rightarrow 0$, $t \rightarrow 0$, and $x \leq kt$ prevail, $\sin \lambda x \rightarrow 0$, $\cos \lambda x \rightarrow 1$, and $\exp(-\lambda^2 Dt) \rightarrow 1$ follow. Therefore, the particular solution (10) reduces to

$$c(x, t) \approx c(0, 0) \cos(\lambda x) \exp(-\lambda^2 Dt) \quad (12)$$

This shows that the corrected form (2) of Babad-Zakhryapina's relation implies concentrations in the lamina because $\cos(\lambda x) \rightarrow 1$ typifies the small system version. Then

a comparison of exponentials reveals the constant λ^2 must be k^2/D^2 . And finally the particular solution becomes

$$c(x, t) \approx c(o, o) \cos \frac{kx}{D} \exp\left(\frac{-k^2 t}{D}\right) \quad (13)$$

The variation of internal composition with distance, which the approximation of reference 1 lacks, appears as a cosine factor. Furthermore, the proper version of Babad-Zakhryapina's expression (2) describes the changes in concentration with time at the interface ($x = 0$) in the small system answer (13):

$$c(o, t) \approx c(o, o) \exp\left(\frac{-k^2 t}{D}\right) \quad (14)$$

In turn, that provides a good estimate of the missing function in the more general Laplace development (5). With the transform of (14),

$$c(o, s) \approx \frac{c(o, o)}{(s + k^2 D)} \quad (15)$$

equation (5) yields

$$c(x, s) \approx c(o, o) \exp \frac{(-x \sqrt{s/D})}{(s + k^2/D)} \quad (16)$$

Reference 3 indicates the inversion as

$$\begin{aligned} c(x, t) \approx \frac{c(o, o)}{2} e^{-(k^2/D)t} & \left[e^{-i(k/D)x} \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} - ik\sqrt{\frac{t}{D}}\right) + e^{i(k/D)x} \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + ik\sqrt{\frac{t}{D}}\right) \right] \approx \frac{c(o, o)}{2} e^{-(k^2/D)t} \left[\cos \frac{k}{D} x \right. \\ & \left. - i \sin \frac{k}{D} x \right] \left(1 - \frac{2}{\sqrt{\pi}} \left\{ \left(\frac{x}{2\sqrt{Dt}} - ik\sqrt{\frac{t}{D}} \right) - \frac{[(x/2\sqrt{Dt}) - ik\sqrt{t/D}]^3}{1!3} + \frac{[(x/2\sqrt{Dt}) - ik\sqrt{t/D}]^5}{2!5} - \dots \right\} \right) \\ & + \left(\cos \frac{k}{D} x + i \sin \frac{k}{D} x \right) \left(1 - \frac{2}{\sqrt{\pi}} \left\{ \left(\frac{x}{2\sqrt{Dt}} + ik\sqrt{\frac{t}{D}} \right) - \frac{[(x/2\sqrt{Dt}) + ik\sqrt{t/D}]^3}{1!3} + \frac{[(x/2\sqrt{Dt}) + ik\sqrt{t/D}]^5}{2!5} - \dots \right\} \right) \end{aligned} \quad (17)$$

The real terms of equation (17) approximate Babad-Zakhryapina's diffusion model. Further reductions of (17) result from the restrictions of the lead paragraph of this section: "For 'low values of k and t ,' as well as for very small $x \leq l = kt$," $\sin kx/D$ and all terms except the first in the erfc expansions approach zero. Thus, the simplified form of the diffusion equation (17) emerges as

$$c(x, t) \approx c(0, 0) \cos\left(\frac{kx}{D}\right) \exp\left(-\frac{k^2 t}{D}\right) \quad (18)$$

which verifies the small system result (13) and reinforces the corrected expression for Babad-Zakhryapina's approximation (2).

In fact, for vanishingly thin films $x \rightarrow kt \rightarrow 0$, $\cos(kx/D) \rightarrow \cos(k^2 t/D) \rightarrow 1$, and $\exp(-k^2 t/D) \rightarrow 1$ all hold. The strengths of the exponential and the cosine effects, however, differ widely:

$$\frac{d \exp(-k^2 t/D)}{dt} = -\frac{k^2}{D} \exp\left(-\frac{k^2 t}{D}\right) = -\frac{k^2}{D} \left(1 - \frac{k^2 t}{D} + \frac{k^4 t^2}{D^2} - \dots\right) \approx -\frac{k^2}{D} \quad (19)$$

$$\frac{d \cos(k^2 t/D)}{dt} = -\frac{k^2}{D} \sin\left(\frac{k^2 t}{D}\right) = -\frac{k^2}{D} \left(\frac{k^2 t}{D} - \frac{k^6 t^3}{3! D^3} + \frac{k^{10} t^5}{5! D^5} - \dots\right) \approx -\frac{k^4 t}{D^2} \quad (20)$$

Thus, as $kt \rightarrow 0$, $\exp(-k^2 t/D)$ changes at least $D/(k^2 t)$ times more rapidly than $\cos(kx/D)$. This means, of course, that the exponential factor dominates the basic diffusion equation at "low values of k and t ." However, Babad-Zakhryapina's presentation failed to show and explain this fact - or even to obtain the proper exponential dependency.

One final point deserves mentioning: Although (13), (17), and (18) are adequate approximations for $k \rightarrow 0$ and $t \rightarrow 0$, substituting $[1 + \cos(kx/D) - \cos(k^2 t/D)]$ for $\cos(kx/D)$ in the equations is more satisfying. And, of course, the added quantity $[1 - \cos(k^2 t/D)] \rightarrow 0$ is a very small time effect compared with $\exp(-k^2 t/D)$ as (19) and (20) testify. Its addition or deletion is well within the allowances of the present estimation. But this change makes (13) and (18)

$$c(x, t) \approx c(0, 0) \left[1 + \cos\left(\frac{kx}{D}\right) - \cos\left(\frac{k^2 t}{D}\right)\right] \exp\left(-\frac{k^2 t}{D}\right) \quad (21)$$

Thus, at the interface $c(o, t) = c(o, o)[2 - \cos(k^2 t/D)] \exp(-k^2 t/D)$, which is smaller than $c(o, o)$ because the exponential decrease overwhelms unity minus the cosine. On the outer surface ($x = l = kt$), however, $c(l, t) = c(o, o) \exp(-kl/D) = c(o, o) \exp(-k^2 t/D)$. This is the correct result indicated by (1) and (2). So, even though (18) and (21) are both reasonable derivations from the model, the latter is better.

IMPLICATIONS

The mass-transport equations developed here reveal space, time trends for fuel-atom concentrations in clads following the model of reference 1. These variations given by a general but complicated relation (eq. (17)) correspond to those obtained with a small-system approximation. Furthermore, a final trivial refinement yields an estimate (eq. (21)) that satisfies all boundary conditions - including the absolute solution for the outer-surface composition.

Compared with the present findings, Babad-Zakhryapina's fuel-component distribution predicts high local concentrations within the clad. Since his equation actually describes only the outside condition (eqs. (A4), (1), and (2)), though, this deviation is intuitively obvious. But when the model operates at the extremes of its assumptions, the simple mass-transport expression of reference 1 is an admissible approximation. This is gratifying because Babad-Zakhryapina's presentation represents a valuable contribution by eight Russian scientists on the "contact diffusion interaction of materials with cladding."

Lewis Research Center,

National Aeronautics and Space Administration,

Cleveland, Ohio, September 16, 1971,

112-27.

APPENDIX - EXCERPT FROM REFERENCE 1, "CONTACT DIFFUSION INTERACTION OF MATERIALS WITH CLADDING"

by A. A. Babad-Zakhryapina

This published work discusses problems arising from diffusion interaction between materials and their claddings and the film of condensate formed on their surfaces. Since condensates practically always form on heated materials, the commencement of interaction is observed during the process of formation of the film. In this connection, the investigation of the characteristics of the diffusion interaction of the film with the materials should be divided into two stages: interaction during the process of the formation of the film and the interaction during process of extended isothermal heating. Detailed results of two stages are presented in this work.

A characteristic of the first stage is the simultaneousness of the course of the two processes: condensation and diffusional transfer of the cladding material into a growing layer. The continuity of the condensate growth, as well as the law governing the growth of the layer itself, gives rise to the appearance of certain specific characteristics in the character of diffusion interaction (Section I).

The interaction of the film with the material during isothermal heating may occur at the expense of a decrease of the content of one of the components of the cladding material and not as a result of the interchange reaction. It is borne out that geometric correlations have a substantial influence on the character of diffusion process in such a system. This is shown by the example of contact diffusion of monocarbide of uranium with molybdenum and tungsten (Section II).

Besides these general questions concerning characteristics of diffusion interaction of deposited materials, investigation is also made of the correlation of the diffusional mobility of atoms with thermodynamic characteristics of materials.

In conclusion, a study is made of data concerning the diffusion of carbon in zirconium carbide (Section III).

1. CHARACTERISTICS OF DIFFUSION PROCESSES IN CONDENSATES, FORMED ON A HOT CLADDING

by A. A. Babad-Zakhryapina and L. Gert

1. Introduction

To create a well bonded layer of condensate with a cladding surface, it is common practice to utilize heating of the cladding during the process of condensation. During the course of the whole process, there occurs an inevitable diffusion interaction between the cladding material and the condensate material, a characteristic of which is a diffusional penetration of the cladding material into the layer of condensate. On the other hand, the penetration of the condensate material into the cladding also, to a certain degree, has to be determined by the conditions of condensation.

The diffusion interaction between the cladding and the condensate may lead to a change in the conditions of condensation, i.e., a change in the character of dependence between the thickness of the layer and the time it takes to form, as well as have a substantial influence on the phase

formation in the condensate layer. Regardless of the fact whether these phenomena are desirable or undesirable in the process of formation of the condensate layer, they have to be taken into account and a method, based on prior knowledge, has to be developed by which the phenomena can be evaluated quantitatively.

2. Unilateral Interaction of the Cladding Material with the Condensate Layer During the Process of the Layer Formation

For the solution of this problem, it is necessary to know the growth law of the condensate layer. Subsequently, two laws will be examined: linear, i.e., the growth of the layer with a constant speed and parabolic - with a variable velocity.

The simplest case, which is encountered in the investigation of the diffusion interaction of the cladding with the condensate, is the unilateral diffusion in the condensate layer. This case may be formulated in the following manner: on a cladding of material A at a temperature T, substance B is placed according to the law $x = f(t)$ (t - time); it is necessary to determine the concentration of substance A (i.e., c_A) on the surface of the layer of condensate.

Here it will be assumed that the coefficient of diffusion A in B (D_{AB}) is considerably greater than the coefficient of diffusion of B in A (D_{BA}). For simplicity and ease of notation, let us consider that $D_{BA} = 0$ and $D_{AB} = D$.

Boundary conditions for this problem have the form (fig. 1) on the interface cladding condensate.

$$c_A \frac{d\ell}{dt} = -D \left(\frac{\partial c}{\partial x} \right)_{c_A}, \quad c(x, t)_{x=0} = c_0$$

on the surface of the layer

$$c(x, t)_{x=\ell} = c_A, \quad \text{where } \ell = f(t)$$

From the general solution of the Fick equation for a unilateral source and above boundary conditions for a case when $\ell = 2b\sqrt{Dt}$, we obtain:

$$c = \frac{c_0}{1 + F(b)} \quad (A1)$$

where $F(b) = \sqrt{\pi} b \exp b^2 \Psi(b)$, $\Psi(b)$ - function of Gauss errors.

Under linear law of growth of layer, when $\ell = kt$

$$c_A = \frac{c_0}{1 + F(k, t)} \quad (A2)$$

where

$$F(k, t) = k \sqrt{\frac{\pi t}{D}} \exp - \frac{k^2 t}{4D} \Psi\left(\frac{\ell}{2\sqrt{Dt}}\right)$$

The expression, determining c_A under linear law of layer growth, is an approximation and may be utilized for calculations at low values of k and t . An accurate solution of this problem may be obtained by the solution of the equation of material balance on the boundary of cladding condensate, where

$$-D \frac{\partial c}{\partial x} \Big|_{x=\ell} = c_A k \quad (A3)$$

bearing in mind that $d\ell/dt = k$.

Let us perform a substitution of variable $k = \ell$. Such a substitution is possible provided that

$$\frac{\partial c}{\partial t} \Big|_{\ell} = \frac{dc_A}{dt}$$

We will prove that the latter equivalence is valid only in the case if $\ell = kt$. Differentiating equation (A3) according to ℓ and comparing the obtained result with the Fick equations for point ℓ , we obtain

$$c_A \frac{d}{d\ell} \left(\frac{d\ell}{dt} \right) = 0$$

As $c_A \neq 0$ according to the problem, then $(d/d\ell) (d\ell/dt) = 0$ which gives $\ell = kt$.

Bearing in mind that $c(\ell, t) = c_A$ and $-D(\partial c_A / \partial \ell) = c_A k$, after transfer to variable "k", we obtain

$$c(x, t) = c_0 \exp\left(\frac{kx}{D}\right) \quad (A4)$$

Let us prove that expression (A4) satisfies Fick's equation and boundary conditions. For this purpose, it is expedient to go to another system of coordinates $X = \ell - x$ (fig. 2). In the new system of coordinates, expression (A4) will be written as

$$c(X, t) = c_0 \exp\left(\frac{kX - k^2 t}{D}\right) \quad (A5)$$

By direct substitution, it is easy to be convinced that expression (A5) satisfies both the Fick equation and boundary conditions.

From equation (A4), it follows that the distribution of the concentration in the layer of the condensate, growing according to linear law, is pseudo-stationary. The form of the concentration curve in this case is determined only by the relationship k/D .

With the increase of the growth rate, the concentration of layers at any one given point, and consequently on the surface, decreases. The same conclusion is arrived at by analysis of approximated correlation (A2).

In any case of parabolic law of growth, c_A remains a constant independent of time while its value is determined only by parameter "b." The above obtained correlations (A3) and (A4) may be utilized for determination of coefficients of diffusion. The most suitable for this purpose is correlation (A4). Conducting a linear interpolation of the concentration curve, which is permissible for lower values of kx/D , we obtain $c(x, t) = c_0 D / (D + kx)$. In this relationship, magnitudes of "k" and "x" are easily determined experimentally. Thus, for computation of D , it is only necessary to know the concentration at any one given point along the thickness of the layer. In the case where, as a result of diffusion, solid solutions are formed and if the concentration dependence of the lattice parameter is known, then the concentration on the surface of the layer can be determined by X-rays.

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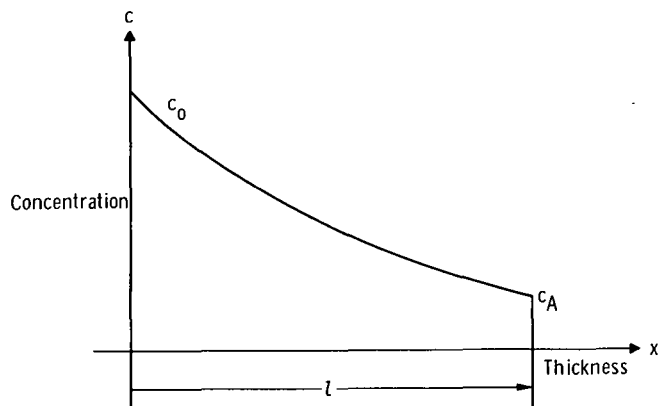


Figure 1. - Diagram of the distribution of concentration in a layer of condensate in a case of unilateral single phase diffusion. (From ref. 1.)

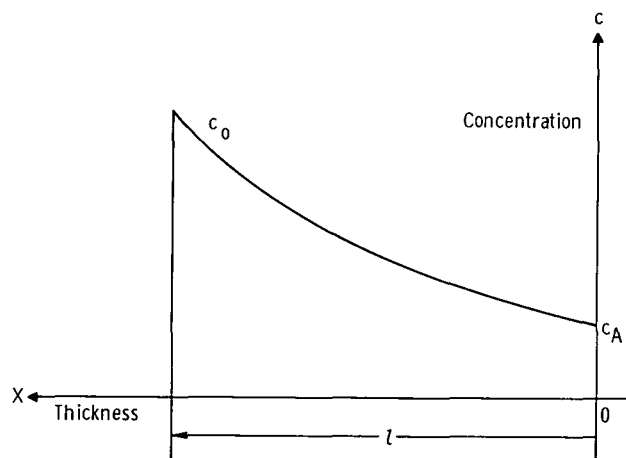


Figure 2. - The connection between systems of coordinates showing the layer on the growth rate under the linear law for the growth of the condensate. (From ref. 1.)



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